Ligand driven assembly of a monoorganooxotin cage from the reactions of organotin precursors with phosphonate ligands

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The reaction of n-BuSn(OH)Cl with t-BuP(O)(OH)2 in a 1:2 ratio in refluxing toluene or stirring in acetonitrile at room temperature forms the monoorganooxotin cage, [(n-BuSn)2O{P(OH)2-t-Bu}]4, I in good yields. The reaction conditions have been varied to optimize the yield of the oxo cluster. An intermediate leading to the formation of I has been identified by 31P NMR spectroscopy. Compound I can be used as a single-source precursor for the formation of SnP2O5 by a low temperature decomposition process at 750°C.

Clusters, cages, rings and coordination polymers containing organotin units are a topic of considerable interest in view of the large structural diversity that exists in these classes of compounds. In the assembly of these compounds, in most instances, the organotin precursor assumes the structure-directing role and steers the reaction towards an eventual product. Thus, the reactivity differences between mono-, di- and tri-organotin precursors towards a common reactant such as a carboxylic acid lead to the formation of varied products whose molecular structures are considerably different. It is surprising to note that such reactivity differences persist even among closely related organotin precursors such as the monoorganotin compounds, n-BuSn(O)OH and n-BuSn(OH)2Cl. Thus, for example, while n-BuSn(O)OH reacts with FeCOOH (Fe=C6H4-Fe=C6H4) to afford a hexameric drum, an analogous reaction of n-BuSn(OH)2Cl affords a tri-nuclear tin derivative whose formation is evidently steered by the phosphonate ligand and not by the organotin precursor. Further, we have carried out a thermolysis of the cage [(n-BuSn)2O{O2P(OH)-t-Bu}]4 and have been able to show that the latter is an excellent single source precursor for the formation of SnP2O5. These aspects are discussed in the following account.

Materials and Methods
n-BuSn(OH), n-BuSn(OH)2Cl and t-butyl phosphonic acid (Aldrich) were used without any further purification. Mono- and disilylated phosphonic acid derivatives were prepared according to literature procedures and were characterized spectroscopically. Melting points were measured using a JSGW melting point apparatus and are uncorrected. Elemental analyses were carried out using a Thermquest CE instruments model EA 110 CHNS-O elemental analyzer. 1H, 31P and 119Sn NMR spectra were obtained on a JEOL-JNM LAMBDA 400 model spectrometer using CDCl3 solutions with the corresponding chemical shifts referenced to tetramethylysilane, 85% H3PO4 and tetramethylin respectively. 31P and 119Sn NMR were recorded under broad-band decoupled conditions. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectropho-
Synthesis of the tetranuclear organotin cage
\[(n\text{-BuSn(OH)}_2 \text{Cl})_4 \] 

1. Reactions of \(n\text{-BuSn(OH)}_2 \text{Cl} \) with \(t\text{-BuP(O)(OH)} \) — Various reactions were carried out in toluene or acetonitrile in varying Sn/P stoichiometric ratios (Table 1). Illustrative procedures are given below.

(a) \(n\text{-BuSn(OH)}_2 \text{Cl} \) and \(t\text{-BuP(O)(OH)} \) were suspended in 100 mL of toluene. The suspension was stirred for 12 h at room temperature by which time the solution became almost clear. Subsequently, the solution was stirred for 12 h at room temperature by which time the white solid had precipitated out of acetonitrile. This was filtered, dried, redissolved (CHCl₃ 30 mL) and filtered again. The clear solution obtained on filtration was reduced to half its original volume and was left undisturbed for 48 h to isolate the product as colorless block-like crystals as indicated by its analytical and spectroscopic data which matched with that obtained in the first preparation (1a).

(b) \(n\text{-BuSn(OH)}_2 \text{Cl} \) and \(t\text{-BuP(O)(OH)(OSiMe}_3\) were taken together in 100 mL of toluene and heated under reflux for 6 h. The work-up of the reaction was performed as detailed above (2a) to obtain 1.

(c) 50 mL of acetonitrile was taken in a 100 mL round-bottom flask to which was charged \(n\text{-BuSn(OH)}_2 \text{Cl} \) and \(t\text{-BuP(O)(OH)} \). The resulting suspension was stirred for 12 h at room temperature at which time a white solid got precipitated out of acetonitrile and was left undisturbed for 48 h at room temperature. Colorless block-like crystals of 1 were isolated.

2. Anal. Calcd. for \(C_{258}H_{116}O_{26}P_{11}Sn_{4} \): C, 31.40; H, 6.60. Found: C 31.50; H, 6.80. \(^1^H\) NMR (CDCl₃, ppm) 0.87 (t, \(-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3\), 12H), 1.10 (d), 1.14 (d) (C-\(\text{CH}_3\)), 72 H), 1.26 (m), 1.36 (m) 1.64 (m) (\(-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3\), 24 H); \(^{31}\text{P}\) NMR (CDCl₃, ppm) 31.1 (\(^{177/179}\text{Sn-O-}^{31}\text{P : 229, 239 Hz})

Powder X-ray diffraction crystallography
Powder X-ray diffractogram was recorded using a Rich Seifert Isodebyflex X-ray unit (model 2002) with Cu Kα radiation and Ni filter.

Results and Discussion
The reactions of \(n\text{-BuSn(OH)}_2 \text{Cl} \) with \(t\text{-BuP(O)(OH)} \) have been carried out under different stoichiometric ratios in various reaction conditions using toluene or acetonitrile as the solvent (Table 1). These reactions proceed with the elimination of hy-
hydrogen chloride and/or water. Surprisingly, none of these reactions needed the assistance of a hydrogen chloride scavenger and cage 1 is almost exclusively formed. The yield of formation of the cage has been optimized (~80%) and the maximum yield is obtained in a reaction involving a 1:2 stoichiometry of the tin and phosphorus reactants. This also corresponds to the actual ratio of these components in the product. Interestingly even in other stoichiometries (1:1, 2:3, 3:4) we were able to isolate only 1 although in slightly reduced yields. The reaction proceeds equally well both in conditions where the water generated in the reaction is removed dynamically (by the use of a Dean-Stark apparatus using toluene as the solvent under reflux conditions; Table 1, entries 2,4,6,8) or where it is left in the reaction medium (Table 1, entries 1,3,5,7,9). Contrary to the formation of the oxo-tin cage 1 in the present instance, in a slightly analogous reaction involving BuSn(OH)2Cl and FeCOOH the isolated product [n-BuSnCl(2-CFc)]2(O)(OH) contains chlorine substituents on tin4. Similarly, the reaction of n-BuSn(OH)2Cl with phosphinic acids also leads to the product which contains chlorine substituents on tin10. Other instances of the formation of various products in reactions of n-BuSn(OH) or n-BuSn(OH)2Cl with a common reagent have been recorded (Table 2).

In order to test the reactivity of the silylated phosphonate ligands, t-BuP(O)(OH)(OSiMe3) and t-BuP(O)(OSiMe3)2 were reacted with n-BuSn(OH)2Cl. High yields of 1 are formed in both of these reactions also by the elimination of trimethylsilylchloride or hexamethyldisiloxane (Table 1, entries 11,12).

It has been reported previously that the reaction of a mixture of n-BuSn(OH) and n-BuSn(OH)2Cl with benzoic acid leads to the formation of a ladder com-

| Table 1—A summary of the reactions of various phosphonate ligands with n-BuSn(OH) and n-BuSn(OH)2Cl |
|---|---|---|---|
| SI No. | Organotin precursors (g) | Phosphonate substrates (g) | Sn:P molar ratio | Experimental conditions | Yield |
| | | | | Solvent | Conditions | Time (h) | g | % |
| 1 | n-BuSn(OH)Cl (1.22) | t-BuP(O)(OH)2(1.37) | 1:2 | toluene | reflux | 6 | 1.80 | 80 |
| 2 | n-BuSn(OH)Cl (1.22) | t-BuP(O)(OH)2(1.37) | 1:2 | toluene | reflux | 6 | 1.81 | 80 |
| 3 | n-BuSn(OH)Cl (1.22) | t-BuP(O)(OH)2(1.37) | 1:2 | acetonitrile | reflux | 6 | 1.78 | 78 |
| 4 | n-BuSn(OH)Cl (1.00) | t-BuP(O)(OH)2(0.84) | 2:3 | toluene | reflux | 6 | 1.18 | 63 |
| 5 | n-BuSn(OH)Cl (1.00) | t-BuP(O)(OH)2(0.84) | 2:3 | acetonitrile | reflux | 6 | 1.21 | 65 |
| 6 | n-BuSn(OH)Cl (1.25) | t-BuP(O)(OH)2(0.94) | 3:4 | toluene | reflux | 6 | 1.32 | 57 |
| 7 | n-BuSn(OH)Cl (1.25) | t-BuP(O)(OH)2(0.94) | 3:4 | acetonitrile | reflux | 6 | 1.36 | 58 |
| 8 | n-BuSn(OH)Cl (1.00) | t-BuP(O)(OH)2(0.56) | 1:1 | toluene | reflux | 6 | 0.80 | 43 |
| 9 | n-BuSn(OH)Cl (1.00) | t-BuP(O)(OH)2(0.56) | 1:1 | acetonitrile | reflux | 6 | 0.76 | 41 |
| 10 | n-BuSn(OH)Cl (0.72) | t-BuP(O)(OH)(OSiMe3) (1.46) | 1:2 | toluene | reflux | 6 | 1.12 | 71 |
| 11 | n-BuSn(OH)Cl (0.89) | t-BuP(O)(OH)(OSiMe3) (1.54) | 1:2 | toluene | reflux | 6 | 1.21 | 73 |
| 12 | n-BuSn(OH)Cl (1.04) | t-BuP(O)(OSiMe3)2 (2.40) | 1:2 | toluene | reflux | 6 | 1.42 | 73 |
| 13 | n-BuSn(OH)Cl2 (0.44) | t-BuP(O)(OH)2 (1.00) | 0.5:0.5:2 | toluene | reflux | 6 | 1.37 | 83 |

* room temperature

Powder X-ray diffraction crystallography
Powder X-ray diffractogram was recorded using a Rich Seifert Jodebyflex X-ray unit model 2002 with Cu Kα radiation and Ni filter.

| Table 2—Various structural forms obtained in the reaction of n-BuSn(OH) or n-BuSn(OH)2Cl with carboxylic and phosphinic acids |
|---|---|---|---|
| SI No. | Ligands | Structural forms on reaction with n-BuSn(OH) | n-BuSn(OH)2Cl |
| | | | | |
| 1 | C6H5-Fe-C6H5-C(O)OH | drum3 | trinuclear cluster4 |
| 2 | (C6H5)2P(O)OH | cube & butterfly11,12 | O-capped cluster10 |
| 3 | Ph2P(O)OH | O-capped cluster13 | extended tetr-nuclear cluster10 |
| 4 | (t-Bu)2P(O)OH | cube12 | crown-butterfly cluster10 |
compound \([n\text{-BuSn(OH)}_2]_2(n\text{-BuSn(Cl)(O_2CPh)}_2)\)_2 containing terminal chlorine atoms, in contrast to the anticipated drum, \([n\text{-BuSn(O)O_2CPh}])\]_2. Accordingly it was of interest to test the reaction of \(t\text{-BuP(O)(OH)}_2\) with a mixture of \(n\text{-BuSn(O)OH}\) and \(n\text{-BuSn(OH)_2Cl}\) to explore if other types of products can be isolated.

However, under these reaction conditions also cage 1 is formed almost exclusively (Table 1, entry 13). Thus, it appears that irrespective of whether \(n\text{-BuSn(OH)_2Cl}\) or \(n\text{-BuSn(O)OH}\) are used as the starting organotin precursors, their reactions with phosphonate ligands leads to the tetranuclear cage 1 as the sole product (Scheme 1). Such an exclusive formation of a single cluster type involving varied reactants, stoichiometries and reaction conditions is quite uncommon in organotin chemistry and points out to the rapid formation of a common intermediate. Although we were unable to obtain unambiguous evidence for the existence of an intermediate species in the present instance, recently we have shown with benzyltin compounds the existence of a half cage \([(\text{PhCH}_2)_2\text{Sn}_2(\text{O}_2\text{P(OH)}-t\text{-Bu})_4]\) that rapidly dimerizes to a tetranuclear cage \([(\text{PhCH}_2)_2\text{Sn}_2(\text{O}_2\text{P(OH)}-t\text{-Bu})_4\text{]}_5\]). It appears that with \(n\)-butyltin derivatives in the present instance the reactivity of such an intermediate is even quicker (Scheme 2).

**Scheme 1**

- (a) solvent/condition-toluene, reflux/CH_3CN, r.t. eliminated products: 6H_2O, 4HCl.
- (b) solvent/condition-toluene, reflux, eliminated products: 4H_2O, 4Me_3SiCl, 2Me_3SiOSiMe_3.
- (c) solvent/condition-toluene, reflux, eliminated products: 2H_2O, 4Me_3SiOSiMe_3.
- (d) solvent/condition-toluene, reflux, eliminated products: 6H_2O, 2HCl.
- (e) solvent/condition-toluene, reflux, eliminated products: 4Me_3SiCl, 6Me_3SiOSiMe_3.

**Scheme 2**

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Fig. 1 — Ia represents the $^{31}$P NMR of a product obtained from the reaction of $n$-BuSn(OH)$_2$Cl and t-BuP(O)(OH)$_2$ in a 1:2 stoichiometry in acetonitrile at room temperature. The reaction mixture was worked up after 4 h of the reaction and the solvent evaporated to give the half-cage 1a. The peaks marked with * represent the half-cage 1a with $^{119}$Sn satellites. Ib shows the $^{31}$P NMR of the cage 1 (after complete conversion) with $^{119}$Sn satellites.

Accordingly, the $^{31}$P NMR spectrum of a product obtained from the reaction of $n$-BuSn(OH)$_2$Cl and t-BuP(O)(OH)$_2$ (1:2, acetonitrile, room temperature, 4h) shows the presence of peaks at 32.8 and 31.2 ppm due to the half-cage 1a (and a small amount of the fully converted cage 1 (Fig. 1a). The phosphorus chemical shifts obtained for 1a closely correspond to the half-cage [[(PhCH$_2$)$_2$Sn$_2$O$_2$P(OH)$_2$]-t-Bu]$_4$ isolated by us recently. 1a rapidly dimerizes to 1 and the $^{31}$P NMR of the latter reveals two resonances at 31.1 and 22.4 ppm (Fig. 1b). These are due to the two different types of phosphorus centers (A and B) involved in bridging the di-tin motifs. The dimerization of 1a to 1 is quite rapid as indicated by our inability to obtain a clean $^{119}$Sn NMR for this intermediate.

The $^{119}$Sn NMR of 1 is shown in Fig. 2 and reveals a triplet of triplets centred at −630.4 ppm. The $^{3}$J(Sn-O-P) values are 239 and 286 Hz. These parameters are similar to those reported previously.

$^{119}$Sn NMR chemical shifts are extremely useful as diagnostic signatures for the various structural forms of organooxotin cages and clusters. Thus, the chemical shift observed for 1 is quite unique and is among the most upfield shifted resonances observed for organotin compounds.

Fig. 2 — $^{119}$Sn NMR of the cage 1 showing a triplet of triplets centered at −630.1 ppm.

Thermal decomposition of Cage 1 to SnP$_2$O$_7$

Although several organooxotin cages have been reported thus far, there have been no attempts to use these as precursors for the generation of materials. Encouraged by the favourable combination of Sn:P ratio as well as the nature of the organic groups in 1 we investigated its thermal decomposition. Thermo-gravimetric analysis of the organooxotin cage 1 was carried out under N$_2$ at a heating rate of 20°C min$^{-1}$ and the curve obtained is shown in Fig. 3.

A three-stage weight loss precedes the final decomposition to afford a stable material. The first two weight losses are gradual while the third is much sharper. The onset of the first weight loss at 270°C is followed by the second loss at 364°C. A gradual decrease in weight continues till 460°C. At this stage the total weight loss is 20.3%. Heating the sample further results in a large weight loss of about 37.3% in the temperature regime of 470-520°C. After this there is
Fig. 3—Thermogravimetric analysis curve of 1.

Fig. 4—Powder XRD pattern for the material obtained on thermolysis of 1.

no further appreciable weight loss even on continuing the heating to 1000°C. At this stage the final char yield is 42%.

The TGA curve can be explained by the following sequence of decomposition steps. The first step is a dehydration involving the elimination of four water molecules from a total of eight P-OH’s present in the cage. The second weight loss is the decomposition of the cage framework leading to the elimination of two molecules of P$_2$O$_5$. The total calculated weight loss corresponding to these two steps is 19.4%, which is very close to the experimental weight loss observed (20.3%). The third and the major event occurs around 470°C and involves the elimination of twelve molecules of i-butene whose calculated weight loss (37.3%) matches the experiment (37%).

To analyze the material formed on thermolysis, cage 1 was calcined independently at 750°C for 15 h in flowing N$_2$. The powder X-ray diffraction pattern (Fig. 4) of the calcined material shows the presence of a predominantly crystalline SnP$_2$O$_7$ phase. The broadening of the powder XRD peaks indicates a small percentage of other unidentified amorphous phases of Sn-O-P networks. FT-IR analysis of the calcined material showed a broad peak centered around 1063 cm$^{-1}$ confirming the presence of Sn-O-P network.

In conclusion, we have shown a ligand driven assembly of the tetranuclear oxotin cage 1 in the reactions of phosphonate ligands with either n-BuSn(O)OH or n-BuSn(OH)$_2$Cl. We have also demonstrated the application of 1 as a single source precursor for SnP$_2$O$_7$ by a low-temperature decomposition process.

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References
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